

REMARKS

Claims 1 and 3-23 are pending. Claims 17 to 22 have been withdrawn from consideration. Claim 1 is being amended by this response. Claims 1, 3-16 and 23 stand rejected for obviousness. Applicants respectfully request reconsideration of the claims in light of the foregoing amendment and the following remarks.

Claim Amendments

Claim 1 has been amended to recites that the emulsion is exposed to actinic radiation falling within a specified range of wavelengths. Support for this amendment is found, for example, on page 10, lines 8-9, of the specification. No new matter has been added by the amendment.

§ 103 Rejection

Claims 1, 3-16 and 23 stand rejected under 35 USC § 103(a) as being unpatentable over von Bonin et al. (USPN 3,255,127), Will (USPNs Re 27,444; 3,256,219; and 3,734,867) in view of Dyer et al. (USPN 5,922,780) or Odian (Principles of Polymerization by Odian, J. Wiley and Sons, 1981, pp. 205-09). These claims have also been rejected as being unpatentable over Dyer alone. Applicants respectfully traverse these rejections as applied to the amended version of the claims.

In order to establish a *prima facie* case of obviousness, the Patent Office must demonstrate that (1) there is a suggestion or motivation in the prior art to modify or combine reference teachings, (2) one skilled in the art would have had a reasonable expectation of success in making the modification or combination, and (3) the prior art reference(s) disclose all of the claim limitations. The fact that one of ordinary skill in the art would have had the capability to modify the method disclosed in the prior art reference(s) is not sufficient. MPEP 2143.01. The prior art reference(s) must provide a motivation or reason for making the changes. MPEP 2142; *Ex parte Chicago Rawhide Manufacturing Co.*, 226 USPQ 438 (PTO Bd. App. 1984). Since, for the reasons explained below, a skilled artisan would not have a reasonable expectation of success in making the combination suggested by the Examiner, and since Dyer alone does not teach or suggest all of the limitations recited in the present claims, the § 103 rejections should be withdrawn.

Rejection of Claims 1, 3-16 and 23 over von Bonin and Will in view of Dyer and/or Odian

As amended, claim 1 recites a polymerization process that utilizes a photoinitiator system and actinic radiation to polymerize an emulsion. With respect to the von Bonin and Will references, the Examiner acknowledges, “these references do not expressly teach use of photoinitiators or combining photoinitiators with other initiators.” (Office Action, p. 2). However, the Examiner asserts that the use of photoinitiators in such systems “would have been clearly obviously for an ordinary artisan for purposes of better reaction control or for purposes of environmental safety, or simply for known functional equivalency of various free-radical polymerization initiators.” *Id.* In support of this position, the Examiner points out that Dyer teaches the use of various initiators for polymerization of water-in-oil emulsions, and that Odian (which is referenced by Dyer) discloses that use of photoinitiators is well known in the art of free radical polymerization. (Office Action, p. 2-3).

Dyer teaches that, in general, “suitable initiators include anionic initiators (e.g., alkyl lithium), cationic initiators (e.g., metal chlorides), coordination catalysts, or free radical initiators.” col. 6, lines 62-64. However, Dyer makes no mention of photopolymerization or the use of photoinitiators. Furthermore, although the Examiner asserts that Odian teaches that photoinitiators may be used in free radical polymerization, Odian fails to teach or suggest the use of photoinitiators to polymerize an emulsion, as is recited in the claims. On the contrary, the chapter on “Emulsion Polymerization” found in Odian (a copy of which is enclosed herewith as Exhibit A¹) has a section entitled “4-3a Initiators” which lists several thermal and redox initiators that may be used for emulsion polymerization but does not identify any photoinitiators that would be suitable for such polymerization. Thus, despite Odian’s general discussion of photoinitiators in the section cited by the Examiner, there is nothing in Odian to teach or suggest that photopolymerization could be used specifically for water-in-oil emulsion polymerization.

Moreover, one skilled in the art would not have had a reasonable expectation of success in photopolymerizing the compositions described in von Bonin, Will and/or Dyer. The Examiner has stated that these references all describe HIPE (high internal phase emulsion) compositions (see 6/29/04, Office Action, p. 3, paragraph 5). HIPE compositions are generally known to be

¹ Exhibit A is taken from third edition of Odian, which may differ from the second edition cited by the Examiner.

opaque or milky in appearance. For example, USPN 5,977,194 (a copy of which is attached hereto as Exhibit B) describes the preparation of a HIPE composition and states that “The resulting emulsion is white and has the consistency of mayonnaise.” (see example 1). Similarly Benson has also described HIPE compositions as having “the consistency of mayonnaise.” (see James R. Benson, “Highly Porous Polymers”, *American Laboratory*, April 2003, p. 4, a copy of which is attached hereto as Exhibit C). Consequently, a skilled artisan would not have had a reasonable expectation of success in using a photoinitiator, such as is described in Odian, to polymerize the von Bonin, Will and/or Dyer compositions, because such HIPE systems are known to be opaque, making the use of photoinitiators difficult.

Rejection of claims 1, 3-16 and 23 over Dyer

The Examiner asserts that “since the claimed process does not contain a drying step to remove the resultant water created within the pores of the polymer the claims read on the uncured polymers produced” by the Dyer process. Applicants disagree. Since the Dyer compositions do not contain a photoinitiator and are not polymerized via exposure of the compositions to actinic radiation, the present claims do not read on Dyer. Although Dyer cites Odian, which describes the use of photoinitiators, it would not be obvious to use photopolymerization to polymerize the Dyer compositions for the reasons discussed above.

Furthermore, the present claims are directed to a “process for making an uncrosslinked polymeric foam.” Applicants have previously pointed out that Dyer, in contrast, describes crosslinked polymers made from polyene monomers such as butadienes, octatrienes and similar conjugated polymers. In response, the Examiner asserts that because Dyer states that the presence of a crosslinker is optional, Dyer also teaches the use of uncrosslinked compositions. Applicants disagree. Monomers used in Dyer belong to a class of monomers which are described in the art as being cross-linking monomers, i.e. they have at least two polymerizing unsaturated groups and thus are able to crosslink even without the addition of another crosslinking agent. For example, USPN 6,323,250 (a copy of which is attached hereto as Exhibit D) states that “aliphatic monomers such as butadiene, isoprene, and pentadiene” are typical examples of cross-linking monomers. (col. 5, lines 29-55). Thus, even when the additional crosslinking agent is omitted from the Dyer compositions they still contain a crosslinker since the Dyer monomers themselves

are capable of crosslinking. Dyer, therefore, fails to describe compositions that have “no effective amount of crosslinking agent” as recited in the present claims.

For the reasons provided above, the rejections of claims 1, 3-16 and 23 under 35 U.S.C. §103 should be withdrawn.

Conclusion

In view of the foregoing amendments and remarks, Applicants respectfully submit that the application is in condition for allowance. Reconsideration of the application is requested.

All communications in this case should be direct to the undersigned. If the Examiner believes a telephone discussion would be helpful to resolve any of the outstanding issue in this case, the Examiner is encouraged to call the undersigned at the number listed below.

Respectfully submitted,

Oct. 11, 2005
Date

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Exhibit A

PRINCIPLES OF POLYMERIZATION

Third Edition

GEORGE ODIAN

The College of Staten Island
The City University of New York
Staten Island, New York



A Wiley-Interscience Publication

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CHAPTER 4

EMULSION POLYMERIZATION

Reaction Time (min)	Conversion (%)
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500	50
700	75
600	40
?	50

Experiment 4. Calculate the rate.

v_p for radical polymerization and ΔS° are given by the equation and 127°C .

Order dependence of the rate on initiator concentration $[I]$. What type(s) of reactions will show the following order dependence?

1. Give rise to these different orders on monomer concentration. Kinetic expressions for R_p and one where R_p is zero.

2. Expected for a low conversion. Explain. Discuss the manner in which size distribution:

3. Lead to a broadening of the size distribution which may be used to determine the mechanism.

4. Methyl methacrylate initiated by azobisisobutyronitrile in benzene at 1 atm and 60°C .

Emulsion polymerization refers to a unique process employed for some radical chain polymerizations. It involves the polymerization of monomers in the form of emulsions (i.e., colloidal dispersions). The process bears a superficial resemblance to suspension polymerization (Sec. 3-13a-3) but is quite different in mechanism and reaction characteristics. Emulsion polymerization differs from suspension polymerization in the type and smaller size of the particles in which polymerization occurs, in the kind of initiator employed, and in the dependence of polymer molecular weight on reaction parameters.

4-1. DESCRIPTION OF PROCESS

4-1a. Utility

Emulsion polymerization was first employed during World War II for producing synthetic rubbers from 1,3-butadiene and styrene. This was the start of the synthetic rubber industry in the United States. It was a dramatic development because the Japanese naval forces threatened access to the natural-rubber (NR) sources, which were necessary for the war effort. Synthetic rubber has advanced significantly from the first days of "balloon" tires, which had a useful life of 5000 mi to present-day tires, which are good for 50,000 mi. Emulsion polymerization is presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylate copolymerizations, and copolymerizations of butadiene with styrene and acrylonitrile. It is also used for methacrylates, vinyl chloride, acrylamide, and some fluorinated ethylenes.

The emulsion polymerization process has several distinct advantages. The physical state of the emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization. The

product of an emulsion polymerization, referred to as a *latex*, can in many instances be used directly without further separations. (However, there may be the need for appropriate blending operations, e.g., for the addition of pigments.) Such applications include paints, coatings, finishes, and floor polishes. Aside from the physical difference between the emulsion and other polymerization processes, there is one very significant kinetic difference. For the other processes there is an inverse relationship (Eq. 3-107) between the polymerization rate and the polymer molecular weight. This drastically limits one's ability to make large changes in the molecular weight of a polymer, from 25,000 to 100,000 or from 100,000 to 25,000. Large decreases in the molecular weight of a polymer can be made without altering the polymerization rate by using chain-transfer agents. However, large increases in molecular weight can be made only by decreasing the polymerization rate by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords the means of increasing the polymer molecular weight without decreasing the polymerization rate. Because of a different reaction mechanism, emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

4-1b Qualitative Picture

4-1b-1 Components and Their Locations

The physical picture of emulsion polymerization is based on the original qualitative picture of Harkins [1947] and the quantitative treatment of Smith and Ewart [1948] with subsequent contributions by other workers [Blackley, 1975; Casey et al., 1990; Fitch, 1980; Gardon, 1977; Hawket et al., 1977, 1980; Piirma, 1982; Poehlein, 1986; Ugelstad and Hansen, 1976]. Table 4-1 shows a typical recipe for an emulsion polymerization [Vandenberg and Hulse, 1948]. This formulation, one of the early ones employed for the production of styrene-1,3-butadiene rubber (trade name: GR-S) is typical of all emulsion polymerization systems. The main components are the monomer(s), *dispersing medium*, *emulsifier*, and water-soluble initiator. The dispersing medium is the liquid, usually water, in which the various components are dispersed by means of the emulsifier. The ratio of water to monomer(s) is generally in the range 70/30 to 40/60 (by weight). The action of the emulsifier (also referred to as *surfactant*

TABLE 4-1 Composition of a GR-S Recipe for Emulsion Polymerization of Styrene-Butadiene^a

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (Dresinate 731)	5
<i>n</i> -Dodecyl mercaptan	0.5
NaOH	0.061
Cumene hydroperoxide	0.17
FeSO ₄	0.017
Na ₄ P ₂ O ₇ · 10 H ₂ O	1.5
Fructose	0.5

^aData from Vandenberg and Hulse [1948].

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is based on the original qualitative atment of Smith and Ewart [1948] Blackley, 1975; Casey et al., 1990; 1980; Piirma, 1982; Poehlein, 1986. ical recipe for an emulsion polym- ormulation, one of the early ones ene rubber (trade name: *GR-S*) is e main components are the mono- r-soluble initiator. The dispersing various components are dispersed onomer(s) is generally in the range sifier (also referred to as *surfactant*

pe for Emulsion

Parts by Weight
25
75
180
5
0.5
0.061
0.17
0.017
1.5
0.5

or *soap*) is due to its molecules having both hydrophilic and hydrophobic segments. Various other components may also be present in the emulsion system. Thus, a mercaptan is used in the above formulation as a chain transfer agent to control the polymer molecular weight. The initiator is the hydroperoxide-ferrous ion redox system and the function of fructose is probably to regenerate ferrous ion by reducing the ferric ion produced in the initiation reaction (Eq. 3-36c). The sodium pyrophosphate acts to solubilize the iron salts in the strongly alkaline reaction medium. The emulsion system is usually kept in a well-agitated state during reaction.

The locations of the various components in an emulsion system will now be considered. When the concentration of a surfactant exceeds its *critical micelle concentration* (CMC), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as *micelles*. The transformation of a solution to the colloidal state as the surfactant concentration exceeds the CMC occurs to minimize the free energy of solution (heat is liberated) and is accompanied by a sharp drop in the surface tension of the solution. Electrical conductivity, ion activities, viscosity, and other solution properties also show marked changes at CMC. CMC values are in the range 0.001–0.1 mole/liter, with most surfactants having values in the lower end of the range. Since surfactant concentrations in most emulsion polymerizations (0.1–3 wt % based on the aqueous phase) exceed CMC by one or more orders of magnitude, the bulk of the surfactant is in the micelles. Typical micelles have dimensions of 2–10 nm ($1 \text{ nm} = 10 \text{ \AA} = 10^{-3} \mu\text{m}$) with each micelle containing 50–150 surfactant molecules. Most authors show the shape of micelles as being spherical, but this is not always the case. Both spherical and rodlike micelles are observed depending on the surfactant and its concentration. The surfactant molecules are arranged in a micelle with their hydrocarbon portions pointed toward the interior of the micelle and their ionic ends outward toward the aqueous phase. The number of micelles and their size depends on the amount of emulsifier. Large amounts of emulsifier yield larger numbers of smaller-sized particles.

When a water-insoluble or slightly water-soluble monomer is added, a very small fraction dissolves in the continuous aqueous phase. The water solubilities of most monomers are quite low, although the spread is large; for example, styrene, butadiene, vinyl chloride, methyl methacrylate, and vinyl acetate are soluble to the extent of 0.07, 0.8, 7, 16, 25 g/liter, respectively, at 25°C [Gardon, 1977]. An additional but still small portion of the monomer enters the interior hydrocarbon portions of the micelles. This is evidenced by X-ray and light-scattering measurements showing that the micelles increase in size as monomer is added. The amount of monomer in micelles compared to that in solution is much greater for the water-insoluble, nonpolar monomers. For example, the amount of micellar monomer is 2-, 5-, and 40-fold larger for methyl methacrylate, butadiene, and styrene, respectively, than the amount in solution [Bovey et al., 1955]. For vinyl acetate, the amount of micellar monomer is only a few percent of that in solution [Dunn, 1985].

The largest portion of the monomer (>95%) is dispersed as *monomer droplets* whose size depends on the stirring rate. The monomer droplets are stabilized by surfactant molecules absorbed on their surfaces. Monomer droplets have diameters in the range 1–10 μm (10^3 – 10^4 nm) or larger. Thus, in a typical emulsion polymerization system, the monomer droplets are much larger than the monomer-containing micelles. Consequently, while the concentration of micelles is 10^{17} – 10^{18} per milliliter, there are at most 10^9 – 10^{11} monomer droplets per milliliter. A further difference between micelles and monomer droplets is that the total surface area of the micelles is larger than that of the droplets by more than two orders of magnitude. The size, shape, and

concentration of each of the various types of particles in the emulsion system are obtained from electron microscopy, light scattering, ultracentrifugation, photon correlation spectroscopy, and other techniques [Debye and Anacker, 1951; Kratochvil, 1964; Munro et al., 1979].

4-1b-2 Site of Polymerization

The initiator is present in the water phase and this is where the initiating radicals are produced. The rate of radical production R_i is typically of the order of 10^{13} radicals per milliliter per second. (The symbol p is often used instead of R_i in emulsion polymerization terminology.) The locus of polymerization is now of prime concern. The site of polymerization is not the monomer droplets since the initiators employed are insoluble in the organic monomer. Such initiators are referred to as *oil-insoluble initiators*. This situation distinguishes emulsion polymerization from suspension polymerization. Oil-soluble initiators are used in suspension polymerization and reaction occurs in the monomer droplets. The absence of polymerization in the monomer droplets in emulsion polymerization has been experimentally verified. If one halts emulsion polymerization at an appropriate point before complete conversion is achieved, the monomer droplets can be separated and analyzed. An insignificant amount (approximately <0.1%) of polymer is found in the monomer droplets in such experiments. Polymerization takes place almost exclusively in the micelles. Monomer droplets do not compete effectively with micelles in capturing radicals produced in solution because of the much smaller total surface area of the droplets.

Polymerization of the monomer in solution undoubtedly takes place but does not contribute significantly, since the monomer concentration is low and propagating radicals would precipitate out of aqueous solution at very small (oligomeric) sizes. The micelles act as a meeting place for the organic (oil-soluble) monomer and the water-soluble initiator. The micelles are favored as the reaction site because of their high monomer concentration (similar to bulk monomer concentration) compared to the monomer in solution. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by the solution of monomer from the monomer droplets. A simplified schematic representation of an emulsion polymerization system is shown in Fig. 4-1. The system consists of three types of particles: monomer droplets, inactive micelles in which polymerization is not occurring, and active micelles in which polymerization is occurring. The latter are no longer considered as micelles but are referred to as *polymer particles*. An emulsifier molecule is shown as $\circ-$ to indicate one end (\circ) is polar or ionic and the other end ($-$) nonpolar.

The mechanism for *particle nucleation* (i.e., formation of polymer particles) proceeds by two simultaneous processes. One is the entry of radicals (either primary radicals or, more likely, oligomeric radicals formed by solution polymerization) from the aqueous phase into the micelles (*micellar nucleation*). The other, *homogeneous nucleation*, involves solution-polymerized oligomeric radicals becoming insoluble and precipitating onto themselves (or onto dead oligomer) [Fitch et al., 1969; Hansen and Ugelstad, 1978]. The precipitated species become stabilized by absorbing surfactant (from solution, monomer droplets, and micelles) and on subsequent absorption of monomer are the equivalent of polymer particles formed by micellar nucleation. The relative extents of micellar and homogeneous nucleation are expected to vary with the water solubility of the monomer and the surfactant concentration. Higher water solubility and low surfactant concentration favor homogeneous nucleation; micellar

Fig.

nucleation is homogeneous nucleation of solution polymerization of monomer. Micellar nucleation is nucleation of monomer in solution. It has been shown that nucleation takes place in the micelles and not in the monomer droplets. The nucleation of monomer in solution is referred to as homogeneous nucleation [Zollner, 1964].

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4-1b-3 Particle Growth

A variety of factors influence the rate of particle growth. Depending on the monomer and surfactant concentrations, the particle growth rate can be controlled. The particle growth rate is also influenced by the surfactant concentration and the monomer solubility.

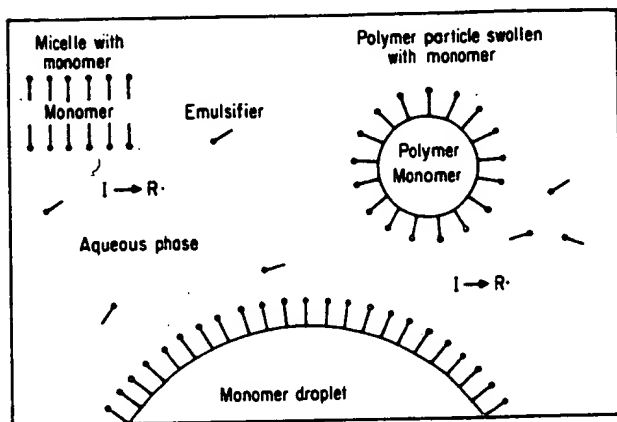


Fig. 4-1 Simplified representation of an emulsion polymerization system.

nucleation is favored by low water solubility and high surfactant concentration. (That homogeneous nucleation occurs is evidenced by the occurrence of emulsion polymerization of systems where the surfactant concentration is below CMC [Roe, 1968].) Micellar nucleation is probably the predominant mechanism for a highly water-insoluble monomer such as styrene [Hansen and Ugelstad, 1979a, 1979b] with homogeneous nucleation the predominant mechanism for a water-soluble monomer such as vinyl acetate [Zollars, 1979].

It has been suggested that the major growth process for the first-formed polymer particles, sometimes referred to as *precursor particles*, is coagulation with other particles and not polymerization of monomer. This coagulation, referred to as *coagulative nucleation*, is then considered as part of the overall nucleation sequence for the formation of *mature* polymer particles whose subsequent growth occurs entirely by polymerization. The experimental evidence for the coagulative nucleation process is the positive skewness of the polymer particle size distribution determined at short reaction times. This indicates that the rate of formation of polymer particles is an increasing function of time that is incompatible with a one-step mechanism but compatible with the two-step process of micellar and/or homogeneous nucleation followed by coagulative nucleation [Feeney et al., 1984]. The driving force for coagulation of precursor particles is their relative instability compared to larger-sized particles. The small size of a precursor particle (several nanometers) with its high curvature of the electrical double layer precludes the high surface charge density required for high colloidal stability. Once the particles reach a larger size with high colloidal stability, there is no longer a driving force for coagulation and further growth occurs only by polymerization.

4-1b-3 Progress of Polymerization

A variety of behaviors are observed for the polymerization rate versus conversion depending on the relative rates of initiation, propagation, and termination, which are in turn dependent on the monomer and reaction conditions (Fig. 4-2). Irrespective of the particular behavior observed, three *intervals* (I, II, III) can be discerned in all emulsion polymerizations based on the *particle number* N (the concentration of poly-

The occurrence of coagulative nucleation does not alter the $\frac{2}{3}$ -power dependence of N on R_i . However, the coagulative nucleation mechanism indicates a more complex dependence of N on S . The exponent of S decreases monotonically from 1.2 to 0.4 with increasing S . The concentration of polymer particles is higher and the nucleation time is longer for systems with high surfactant concentrations. Polymer particle formation becomes less efficient at longer times as there is a greater tendency for capture of precursor particles by polymer particles when the latter concentrations are high. Within the overall behavior predicted by Eq. 4-11, there is compatibility with the $\frac{2}{3}$ -power dependence of N on R_i predicted by the Eq. 4-10.

Nonpolar monomers such as styrene, with little tendency toward radical desorption, generally show $\frac{2}{3}$ - and $\frac{1}{2}$ -power dependencies of N on S and R_i , respectively. This result, however, cannot be taken to exclude coagulative nucleation since one cannot preclude the exponent of the dependence of N on S being larger and smaller, respectively, than $\frac{2}{3}$ at lower and higher concentrations of surfactant than those studied. Monomers such as vinyl acetate and vinyl chloride, which show Case 1 behavior, tend to show a dependence of N on S in line with that predicted by Eq. 4-11, indicating the presence of coagulative nucleation. Simultaneously, the dependence of N on R_i deviates markedly from Eq. 4-11. When extensive radical desorption occurs, the large fraction of nucleation is initiated by desorbed radicals with the result that N is little affected by R_i . Thus, the order of dependence of N on S is 0.64 for styrene, 0.86 for methyl methacrylate, 1.0 for vinyl chloride, and 1.0 for vinyl acetate, while the orders of dependence on R_i are 0.36, 0.20, 0, and 0, respectively [Hansen and Ugelstad, 1979a, 1979b]. The emulsion copolymerization of acrylonitrile and butyl acrylate shows a decrease in the exponent of the dependence of N and S from 0.67 to 0.40 with increasing surfactant concentration when an anionic surfactant was used [Capek et al., 1988]. The exponent was close to one for polymerization in the presence of a cationic surfactant.

Anomalous results have been observed in some emulsion polymerizations—inverse dependencies of N , R_p , and \bar{X}_n on surfactant concentration. Some surfactants act as inhibitors or retarders of polymerization, especially of the more highly reactive radicals from vinyl acetate and vinyl chloride [Okamura and Motoyama, 1962; Stryker et al., 1967]. This is most apparent with surfactants possessing unsaturation (e.g., certain fatty acid soaps). Degradative chain transfer through allyl hydrogens is probably quite extensive.

The polymer particles decrease in stability during Intervals II and III since the total polymer particle surface area increases and the coverage of the surface with surfactant decreases. The relative decrease in particle stability appears to be insufficient to cause coalescence as long as stirring is maintained since N is generally observed to be constant. In some systems, however, the stability decreases sufficiently to cause the particles to coalesce and N decreases with conversion [Blackley, 1975].

4-3 OTHER CHARACTERISTICS OF EMULSION POLYMERIZATION

4-3a Initiators

The initiators used in emulsion polymerization are water-soluble initiators such as potassium or ammonium persulfate, hydrogen peroxide, and 2,2'-azobis(2-amidino-propane) dihydrochloride. Partially water-soluble peroxides such as succinic acid peroxide and *t*-butyl hydroperoxide and azo compounds such as 4,4'-azobis(4-cyanopen-tanoic acid) have also been used. Redox systems such as persulfate with ferrous ion

not alter the $\frac{2}{3}$ -power dependence of mechanism indicates a more complex increases monotonically from 1.2 to 0.4. r particles is higher and the nucleation concentrations. Polymer particle formation there is a greater tendency for capture than the latter concentrations are high. 4-11, there is compatibility with the $\frac{2}{3}$ -Eq. 4-10.

little tendency toward radical desorption. N on S and R_i , respectively. This results in no nucleation since one cannot preclude growing larger and smaller, respectively, than the surfactant than those studied. Monomers such as styrene show Case 1 behavior, tend to show a behavior predicted by Eq. 4-11, indicating the presence of a dependence of N on R_i deviates markedly from the dependence occurs, the large fraction of monomer with the result that N is little affected by surfactant. S is 0.64 for styrene, 0.86 for methyl methacrylate, 0 for vinyl acetate, while the orders of magnitude are respectively [Hansen and Ugelstad, 1979]. Acrylonitrile and butyl acrylate shows a dependence of N and S from 0.67 to 0.40 with increasing surfactant used [Capek et al., 1988]. The effect of surfactant on polymerization in the presence of a cationic surfactant

some emulsion polymerizations—inverse concentration. Some surfactants act especially of the more highly reactive radicals (Miyazawa and Motoyama, 1962; Stryker et al., 1962) possessing unsaturation (e.g., certain monomers) through allyl hydrogens is probably quite

ty during Intervals II and III since the coverage of the surface with surface stability appears to be insufficient to maintain since N is generally observed to decrease sufficiently to cause conversion [Blackley, 1975].

EMULSION POLYMERIZATION

ization are water-soluble initiators such as hydrogen peroxide, and 2,2'-azobis(2-amino-2-methylpropane) and other water-soluble peroxides such as succinic anhydride peroxide and other water-soluble compounds such as 4,4'-azobis(4-cyanopentanoic acid) and other water-soluble systems such as persulfate with mercap-

(Eq. 3-38a) are commonly used. Redox systems are advantageous in yielding desirable initiation rates at temperatures below 50°C. Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite, or bisulfite ion.

4-3b Surfactants

Anionic surfactants are the most commonly used surfactants in emulsion polymerization [Blackley, 1975; Gardon, 1977]. These include fatty acid soaps (sodium or potassium stearate, laurate, palmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate). The sulfates and sulfonates are useful for polymerization in acidic medium where fatty acid soaps are unstable or where the final product must be stable toward either acid or heavy-metal ions. Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjunction with anionic surfactants for improving the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution. The presence of the nonionic surfactant imparts a second mode of colloidal stabilization, in addition to electrostatic stabilization by the anionic surfactant, via steric interference with the van der Waals attraction between polymer particles. Nonionic surfactants are also of use where the final polymer latex should be insensitive to changes in pH over a wide range. Nonionic surfactants are only infrequently used alone, since their efficiency in producing stable emulsions is less than that of the anionic surfactants. Anionic surfactants are generally used at a level of 0.2–3 wt % based on the amount of water; nonionic surfactants are used at the 2–10% level. Cationic surfactants such as dodecylammonium chloride and cetyltrimethylammonium bromide are much less frequently used than anionic surfactants because of their inefficient emulsifying action or adverse effects on initiator decomposition. Also, cationic surfactants are more expensive than anionic surfactants.

Surfactants increase particle number and decrease particle size as their concentration in the initial reaction charge is increased. However, one can use delayed addition of surfactant after nucleation is complete to improve particle stability, without affecting the particle number, size, and size distribution.

3c Other Components

The quality of the water used in emulsion polymerization is important. Deionized water may be used since the presence of foreign ions or ions in uncontrolled concentrations can interfere with both the initiation process and the action of the emulsifier. Antifreeze additives are used to allow polymerization at temperatures below 0°C. These include inorganic electrolytes as well as organics such as ethylene glycol, glycerol, methanol, and monoalkyl ethers of ethylene glycol. The addition of inorganic electrolytes often affects the polymerization rate and stability of the emulsion. Sequestering agents such as ethylenediamine tetraacetic acid or its alkali metal salts may be added to help solubilize a component of the initiator system or to deactivate traces of calcium and magnesium ions present in the water. Buffers such as phosphate or borate salts may be used to stabilize the latex toward pH changes.

Propagation and Termination Rate Constants

on polymerization proceeds in a polymer particle where the concentration of is quite high throughout the reaction. This type of system is then similar to

Highly Porous Polymers

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INTRODUCTION

Porous polymers have been around for many decades. A typical porous polymer is prepared by co polymerizing styrene and divinylbenzene ("DVB") resulting in formation of very small pores ("micropores") as a result of DVB tying together linear chains of styrene at various points (see Figure 1). The "degree of cross-linking" is the percentage of DVB present, and this determines the size of the pores. Thus, a 10% cross-linked polymer contains 10% DVB and has somewhat smaller pores than a 2% cross-linked polymer since the additional DVB creates additional linkage points making the average distance between those points smaller. However, as cross-linking is reduced to increase pore size, the physical stability of the polymer decreases. These polymers cannot withstand much pressure before they collapse. Pore sizes are typically less than 30 Å in diameter although pore size distributions are fairly uniform. These low cross-linked polymers are often referred to as "gels".

Another type of porous polymer was independently developed in the late 1950s by scientists at The Dow Chemical Company and at Rohm and Haas. Subsequently, patents were issued to Alfrey and Lloyd [1] and to Meitzner and Oline [2]. These materials have come to be called "macroporous polymers", and pores are formed independently of cross-linking (see Figure 2). Polymerization takes place in the presence of "porogens". Porogens are substances that are soluble in monomers, but insoluble in formed polymers. Thus, as polymerization proceeds, pores are formed in the spaces where porogens are found. Pore diameters are typically greater than 50 Å, with some polymers having pore diameters as great as 2000 to 4000 Å. Most polymers, however, contain pores in the 100 Å to 300 Å range. Pore size distributions tend to be somewhat broad, particularly in polymers having large average pore sizes. These materials are characterized by irregular-shaped pores that terminate within the polymer body. Macroporous polymers are usually prepared with a high degree of cross-linking (typically 30% or greater) to lend greater physical stability to the resulting material and to yield polymers that do not swell in solvents. The discovery of this route to synthesizing polymers led to materials with much larger pore size and much higher porosity than preceding microporous materials; however total porosity rarely exceeds 50%.

Nearly all porous polymer particles produced in the last fifty years are either gels or are macroporous polymers prepared using the method described above. These materials have found numerous uses in a wide range of commercial products including ion-exchange applications, supports for liquid chromatography, metal recovery, and cosmetics. Until recently, there have been

no advances in this technology and pore size and morphology have remained unchanged for these several decades.

h

In 1985, Barby and Haq of Unilever successfully developed porous polymer structures that are distinct from macroporous polymers of prior decades [3]. These materials are known as “high internal phase emulsions” (“HIPE”). HIPE structures had been of interest to chemists and materials scientists for many years, but they were difficult to study because they were unstable. Unilever’s methods of stabilizing these emulsions and finally, polymerizing them has lead to materials of unusual and useful properties. HIPE structures are characterized by the presence of very large pores of micrometer dimensions (“cavities”) as opposed to pores associated with microporous or macroporous polymers having only Angstrom dimensions. Furthermore, these large cavities are interconnected by a series of smaller pores, thereby enabling each to communicate with those adjacent.



Figure 1 Microporous polymer. These polymers are formed by cross-linking linear chains of monomer. Cross-links (shown as heavy lines above) create very small pores within the three-dimensional matrix. Known as “gels”, these polymers are soft and compress under pressure.



Figure 2. Macroporous polymer. These materials have a high degree of cross-linking, preventing them from swelling in solvents. Pores are larger than gels, but are irregular and terminate inside the matrix. Total pore volumes are typically 50%.

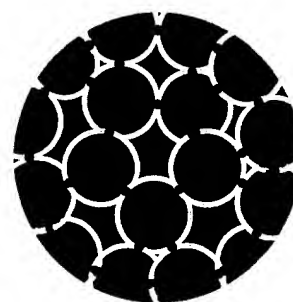


Figure 3. High internal phase emulsion. HIPE polymers, illustrated above, contain extremely large cavities that are interconnected. Cavities are of micrometer dimensions, rather than angstrom dimensions of conventional polymers. Total pore volume can exceed 90%.

In 1996, Li and Benson of Biopore Corporation advanced this technology and succeeded in producing HIPE polymers as distinct, spherical particles [4]. (Unilever’s approach yielded polymers in blocks.) These spheres exhibit the same physical characteristics of the original Unilever material in that they are composed of large, micrometer-size cavities that are interconnected by smaller pores. The polymers are further characterized by especially high porosity with void volumes in the range 70% to 90%. This results in a highly permeable structure that gives a low-density product. A photograph of this unique morphology is shown in Figure 4.

This paper examines these new high internal phase emulsion polymers, and discusses their properties and potential applications.

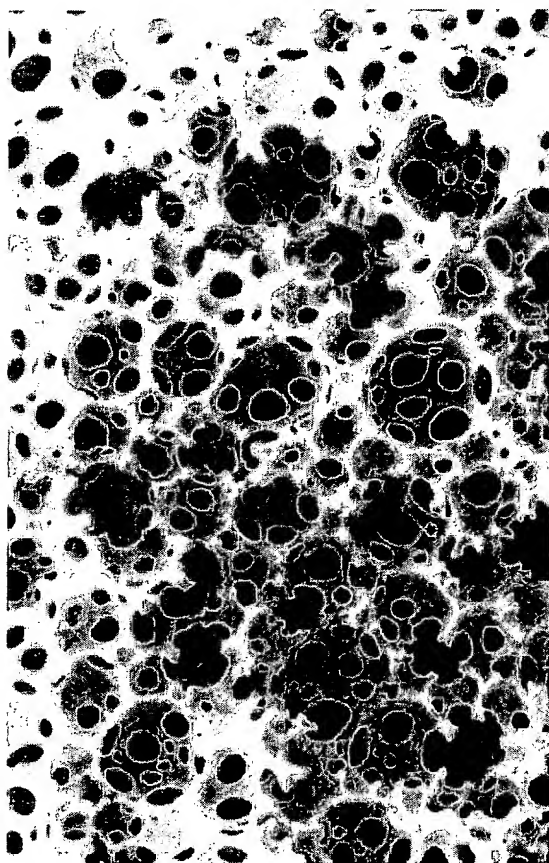


Figure 4. Electron Micrograph of Internal Structure. Note the very large cavity diameters. These can be as large as 50 μm . Interconnecting pores are readily visible and show each cavity internally connected to those adjacent. This structural regularity is unusual in polymers and can lead to numerous products with useful commercial applications.

PREPARATION

Both microporous and macroporous polymers described above are prepared by a *suspension polymerization* technique. This is a process by which oil in water suspensions are achieved by rapidly stirring liquid monomers (the oil phase) along with a dispersing agent in a large amount of water. Droplets of monomers are formed and are stabilized by the dispersing agent. If the monomer mixture also contains a polymerization initiator, a porous polymer is formed as reaction temperature increases to the initiator's activation temperature. HIPE spheres are also prepared using suspension polymerization, but the starting material is not liquid monomers. Before the suspension polymerization can occur, unique HIPE structures must be prepared in a separate, preliminary step.

HIPE structures are formed when an oil, water and suitable emulsifier are mixed with agitation. The water becomes dispersed in the oil phase and as its concentration increases, the consistency of the mixture changes to a thick liquid. At even higher levels of water, above 70%, the mixture adopts the consistency of mayonnaise. This resulting substance is the high internal phase emulsion and is quite stable. It can then be suspended in a large amount of water in the presence of an appropriate surfactant, and spheres of HIPE are formed. The end result is a three-dimensional structure containing interconnected cavities having chemical properties of styrene (or whatever monomers were chosen), but unique physical properties. These spheres of HIPE are called "*Cavilink*TM"[5].

Adjusting phase volume can modify morphology. It is possible to influence density, surface area and cavity size, for example. *Cavilink* polymers have a microstructure that is highly permeable. Permeability increases with the size of interconnects and has been shown to have up to five times higher permeability than commercial materials at equivalent pore rating. The range of typical properties of *Cavilink* materials is summarized in Table 1.

It is important to recognize that this technology does not modify chemical characteristics of polymers, only the physical characteristics. Monomers chosen to polymerize as spherical HIPE materials do not undergo any chemical changes during synthesis. Thus, any known chemical modifications of conventional polymers can be applied to HIPE polymers.

Property	Measurement/Description
Density (typical)	0.05 g/cm ³ to 0.2 g/cm ³
Internal void volume	70% to 90%
Cavity diameter range	1 µm to 50 µm
Interconnect pore diameter	Variable, from small pores to a maximum of 20% of cavity diameter
Surface area	2 - 30 m ² /g

Table 1. Typical properties. One characteristic of high internal phase emulsion polymers is large pore volume, up to 90%. This provides exceptional absorption capabilities as well as permitting materials to act as carriers of active ingredients. Large micrometer-size cavities of *Cavilink*, unique among porous polymers, allow retention and/or transport of large molecules such as proteins or nucleic acids or even of whole cells or viruses.

COMMERCIAL POROUS POLYMERS

Comparison of *Cavilink* morphology with conventional materials illustrates its unique features. Figures 5 – 7 are electron micrographs of some commercial porous polymers with their distinctive "cottage cheese" appearance. Figure 5 is an SEM photo of a MicrospongeTM polymer manufactured by Advanced Polymer Systems, Inc. Note the amorphous structure in the sphere interior. Figure 6 is an SEM photo of a macroporous polymer particle manufactured by Rohm & Haas ("Amberlite®"). These commercial products should be compared with Figure 7 that shows *Cavilink* microstructure. *Cavilink*'s morphology is clearly differentiated, characterized by the regularity of its cavities, much larger cavity diameters and clearly visible interconnecting pores. Conventional porous polymers exhibit an amorphous structure, clearly lacking the internal regularity of

Cavilink. The largest pore diameter obtained in manufacturing conventional porous polymers is about 4000 Å [6], with most materials having pore diameters of 100–300 Å. In contrast, the *smallest* cavity diameter of *Cavilink* spheres is about 10,000 Å.

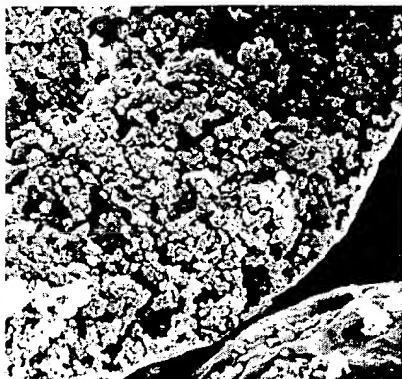


Figure 5. SEM of typical porous polymer. Note the amorphous, “cottage cheese” appearance. The “skin” visible on the surface would actually limit the material as an absorbent since it permits only very small molecules to permeate its surface.

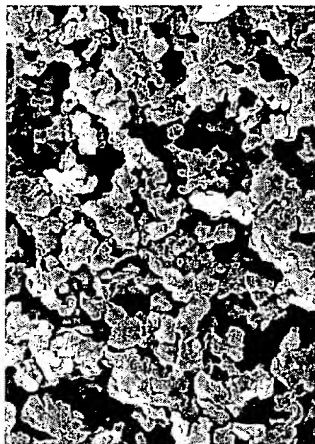


Figure 6. Amberlite® polymer. Manufactured by Rohm & Haas, this is typical of conventional “macroporous” polymers that feature amorphous internal structures characterized by irregular pores.

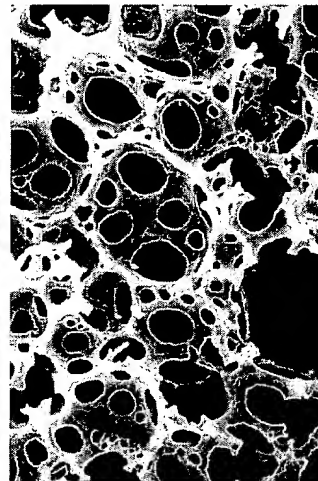


Figure 7. SEM of Cavilink polymer. Clearly distinguished from Figures 5 and 6, this new polymer exhibits much larger cavities and a fully interconnected network.

Cavilink polymers are easily distinguished from conventional microporous and macroporous polymers. Figure 8 illustrates a commercial porous polymer from Advanced Polymer Systems. In contrast, Figure 9 shows a *Cavilink* sphere with open cavities fully communicating with the sphere surface. A broken sphere of *Cavilink* is shown in Fig. 10 illustrating that there is little difference between surface and internal morphology of these polymers.

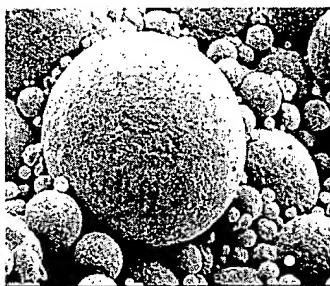


Figure 8. Conventional porous polymer surface. This photograph illustrates an Advanced Polymer Systems product. Note the relatively smooth surface. Internal porosity (as illustrated in Fig. 5) does not always communicate with the surface with this type of technology.

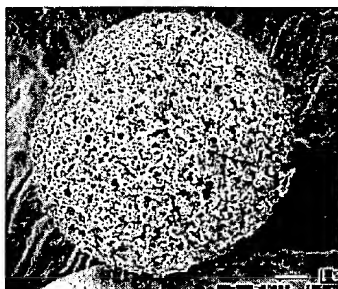


Figure 9. Cavilink polymer with fully open surface. This SEM photo shows distinctive regularity of cavities in *Cavilink* polymers. Cavities have diameters greater than 10,000 Å. Higher magnifications reveal characteristic interconnected structure, (see Fig. 7).

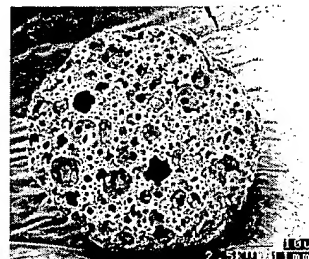


Figure 10. Broken sphere of Cavilink polymer. This is interior of polymer type shown in Fig. 9 and shows cavities and pores fully communicating with sphere surface. Interconnected cavities are not present in conventional macroporous polymer products such as shown in Fig. 8.

CAVILINK MICROSTRUCTURE AND COMPOSITION

Internal microstructure of *Cavilink* polymers remains relatively uniform and is characteristic of polymers prepared using this technology. Interconnecting pore size can be varied from rather small pores to pores as large as 20% of cavity diameters. Porosity of the thin membranes that form cavity walls can also be controlled. Figures 11 and 12 illustrate this principle. Figure 11 shows a cavity wall that is relatively “solid”; whereas Figure 12 shows a cavity wall that itself contains micropores. Note, however, that spheres having highly porous walls such as illustrated in Figure 12 are extremely fragile.

Although polymers illustrated thusfar comprise poly(styrene-divinylbenzene), many other polymer compositions are possible. It is important to recognize that this technology defines *morphology* of polymers, and is not necessarily dependent upon polymer composition. For example, it is straightforward to prepare these HIPE polymers from methylmethacrylates and related materials. Of course, it is also possible to chemically modify polymer surfaces using conventional chemistry after HIPE polymers are prepared. For example, sulfonation, amination or similar modifications of polystyrene HIPE polymers are easily accomplished. In fact, such reactions are expected to be more efficient since the entire surface of *Cavilink* polymers is available to reactants as they pass through interconnecting pores.

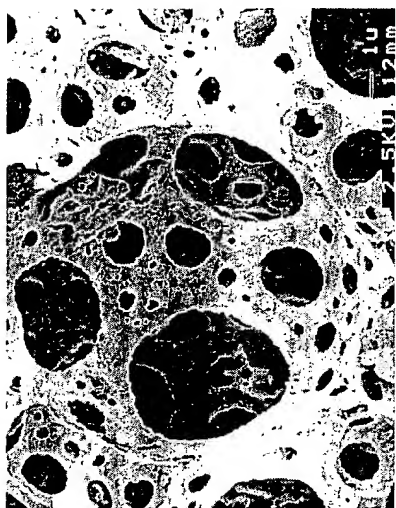


Figure 11. Microstructure of walls. “Membranes” that separate large cavities and provide interconnecting pores can also be controlled using HIPE technology. This figure illustrates relatively solid membrane wall. Figure 12 illustrates material with highly porous membrane walls.

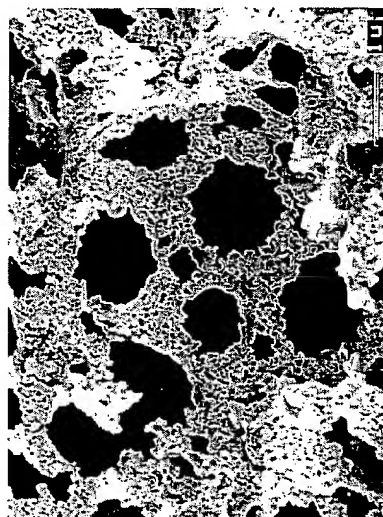


Figure 12. Wall of cavities can also be porous. This photograph reveals an even more porous microstructure than shown in Figure 11. HIPE technology offers a great deal of flexibility in creating polymer morphologies.

It is also possible to carbonize *Cavilink* polymers without losing their interconnected cavity structure. Figure 13 illustrates a carbonized version of *Cavilink* and shows internal morphology was not altered by carbonization.

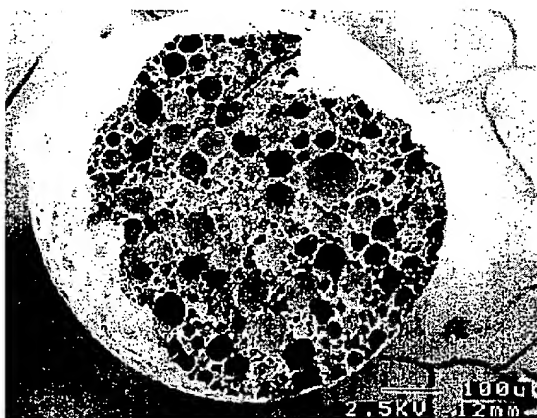


Figure 13. Carbonized Cavilink. This unusual material, composed of pure carbon, retains characteristic morphology of interconnected cavities central to this technology. This SEM photograph illustrates that underlying morphology is unchanged by carbonization processes. Carbonized polymers may be particularly useful in adsorption applications where very fast kinetics is desired, or where the open carbon framework is filled with an active ingredient such as a catalyst. Communicating cavities allow much faster access to interior surfaces or cavity contents than conventional porous polymers.

HYDROPHILIC CAVILINK POLYMERS

In 2000, Kitagawa extended HIPE technology to allow production of polymers produced from entirely hydrophilic monomers [7, 8]. *Cavilink* polymers discussed above were prepared from hydrophobic monomers such as styrene or methylmethacrylate. Kitagawa discovered processes that allowed synthesis of HIPE spheres comprising monomers that are soluble in water. His process yields interconnected porous structures that are themselves hydrophilic. Such polymers find applications in consumer, industrial and biomedical markets. Some examples are shown in Figures 14 – 16.

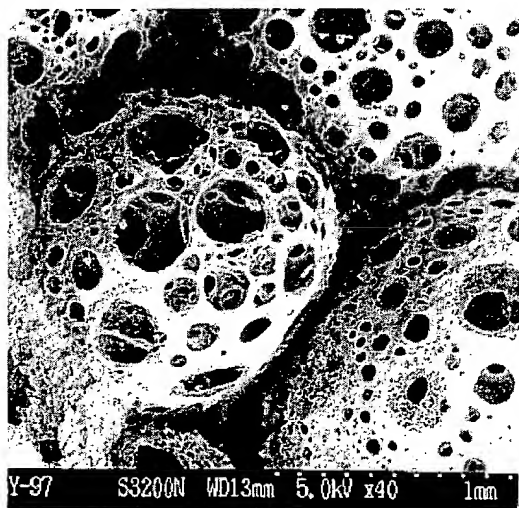


Figure 14. SEM photo of hydrophilic Cavilink polymer. This material is a low cross-linked polyacrylic acid, polymerized as spheres, and comprised of large cavities interconnected by smaller pores. This unique physical structure imparts special properties to the polymer (see text).

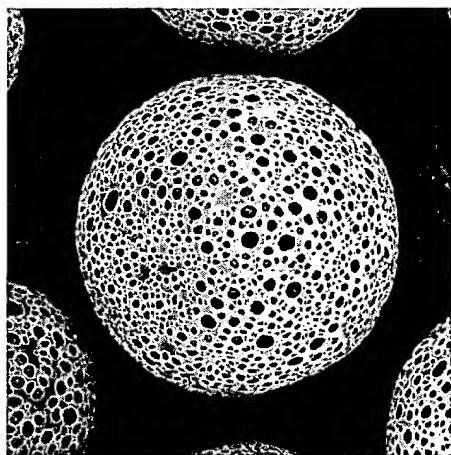


Figure 15. Hydrophilic HIPE polymer. Manipulation of polymerization conditions yields polymer materials of various morphologies. This SEM photo shows cavities of somewhat smaller diameters than illustrated in Figure 14 above.

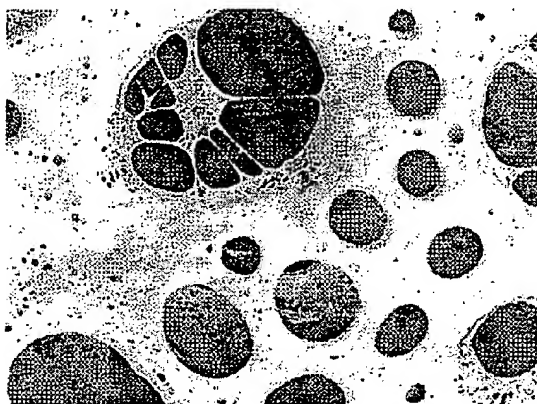


Figure 16. SEM of sphere surface. Surface cavities are visible, and interconnected regions can be seen within some cavities. When dry, the polymer surface appears solid, but when hydrated, these materials can expand with absorption of water.

Polymerization in this unique morphology does not alter chemical properties since chemical composition of the monomers is not affected in manufacturing processes; however, physical properties are changed. Resulting products exhibit a highly permeable structure that is easily dried to give a low-density material. Interconnecting pores allow liquids to flow through and rapidly fill the cavities. As absorbents, *Cavilink* polymers are superior to existing commercial products. Figure 17 illustrates the kinetics of liquid uptake of a hydrophilic *Cavilink* polymer compared with a commercial product from Dow Chemical Company. Both materials are cross-linked polyacrylic acid.

Figure 17 shows the total amount of 0.9 % saline solution absorbed by *Cavilink* product is about twice that of the commercial material, and complete uptake is completed in only a few seconds rather than a few minutes. It is speculated that this improvement in kinetics is due to the large, vacant cavities present in *Cavilink*. As the polymer membrane on the surface of the spheres is wetted, it rapidly expands, creating a vacuum in the cavities. This vacuum quickly draws liquid into those empty chambers, thereby wetting cavity walls. This creates a vacuum in adjacent cavities, further accelerating the process of absorption. Thus, fluid wets and expands the low cross-linked polymer membrane, fills empty cavities, and substantially increases the amount of liquid absorbed into the matrix.

As with hydrophobic polymers discussed earlier, hydrophilic technology is not limited to specific monomers. Methods of preparation allow many hydrophilic monomers to be utilized. Numerous materials, including polymers that are biodegradable, can be prepared in this morphology.

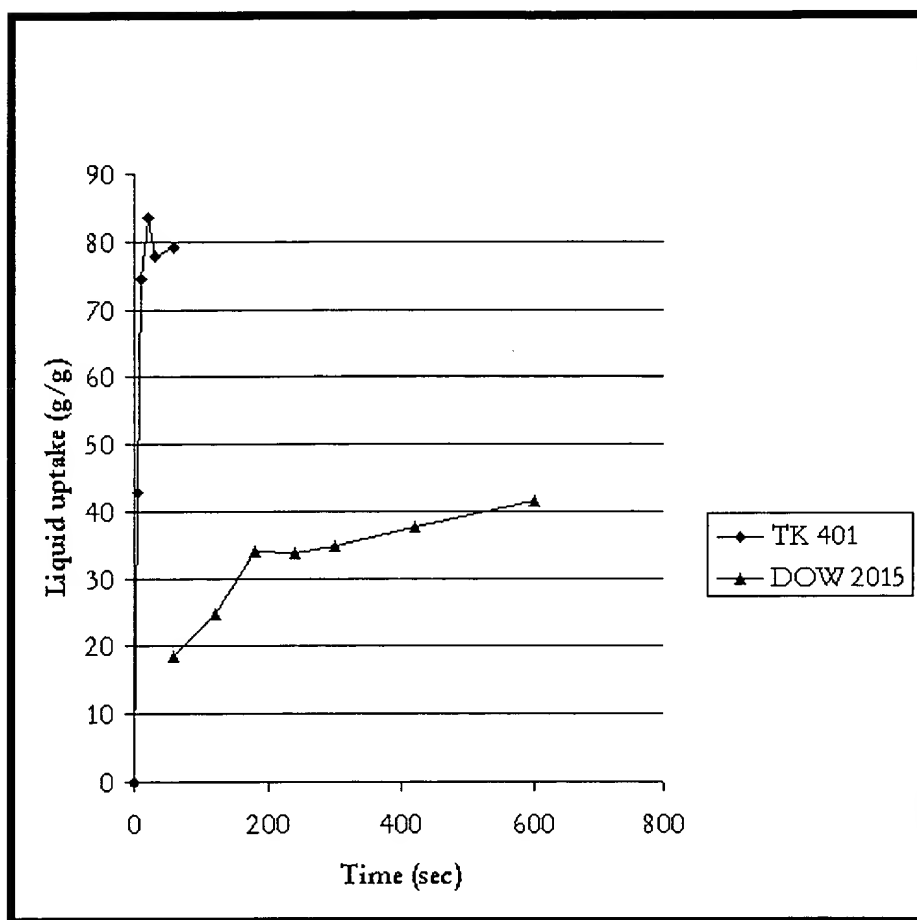


Figure 17. Kinetics of liquid uptake. Comparison of a *Cavilink* superabsorbent polymer with commercial product from Dow Chemical Company illustrates substantially improved rate of uptake of liquid. Both materials are polymers of cross-linked polyacrylic acid, but the *Cavilink* polymer is prepared in the HIPE morphology (see Figures 14 – 16). Changing morphology without altering chemical composition imparts new physical properties to polymers. Liquid chosen for this comparison is 0.9% aqueous sodium chloride.

DISCUSSION

An important feature of this technology is its versatility in allowing construction of a wide range of physical and chemical properties. There are few limits on selection of hydrophilic or hydrophobic monomers for polymerization in these unique forms, so virtually any type of chemical property can be achieved. Alternately, structures can be chemically modified after polymerization in ways similar to other polymers having that chemical composition. All finished materials will have chemical characteristics of underlying polymers, but physical properties will be dramatically changed.

Spheres can be made rigid, fragile, rubbery, sponge-like or soft. Spheres can be made to swell a great deal as indicated in the discussion above for superabsorbent applications, or they can be made to swell not at all in applications where expansions in volume are inappropriate. Spherical cavities within polymers, being of micrometer dimensions, can be utilized as chambers for containing liquids, living cells, viruses, enzymes, microorganisms or even solid particles. Some properties of HIPE polymers that can be influence in manufacturing are summarized in Table 2.

Property	Control Range
Sphere diameter	40 μm to $>1000 \mu\text{m}$
Cavity diameter	less than 1 μm to 50 μm
Interconnecting pore diameter	variable, from very small to 20% of cavity diameter
Porosity of membrane walls	solid to highly porous
Surface	communicates to interior; cavity size can be controlled
Surface chemistry	whatever is possible with native polymer
Polymer composition	many monomers possible
Carbonization	carbonization possible

Table 2. Properties of Cavilink. Properties of *Cavilink* polymers that can be controlled or influenced via the manufacturing processes described in the text.

Applications for *Cavilink* materials cover diverse markets from high technology biomedical and biotechnology applications to industrial processes and consumer goods. The most interesting applications exploit the unique aspects of micrometer-size, interconnected cavities that characterize these materials. Following is a brief discussion of some applications that successfully incorporate these features.

Cell Culture Applications. In 1992, Lee *et al.* described successful utilization of HIPE materials as cell culture media [9]. Their work showed that micrometer-size cavities could be used to contain whole cells and allow them to proliferate. This application could be extended to virus production in development of vaccines for both human and animal use. Cells may be bound internally in *Cavilink* cavities, fed nutrients through interconnecting pores, and allowed to produce virus particles that would migrate outward. In general, vaccine production utilizes cells that require microcarriers for growth in cell culture tanks. Microcarriers have the advantage of protecting cells from shear stresses of bioreactors and enabling higher concentrations of cells, with concomitant economic benefits.

Gene Therapy. As discussed above, cavities of *Cavilink* polymers are of micrometer dimensions and are sufficiently large to contain whole virus particles. As such, spheres of these polymers could be used in gene therapy applications to deliver viral vectors to target cells. In 2001, Cavanagh *et al.* described experiments whereby DNA information was injected into target cells via viral vectors that were "hidden" within *Cavilink* particles [10]. It is expected that placing gene-modified viruses into carrier polymers will provide some protection against immune systems of hosts, thereby allowing successful migration of those viruses to target cells.

Immobilized Enzymes. The large cavities characteristic of this technology seem ideally suited as solid supports for enzyme immobilization applications. Steric hindrance impairs conventional porous materials, but micrometer-size cavities of *Cavilink* polymers allow substrates full access to active regions of enzymes and interconnecting pores provide clear egress to enzyme-substrate products. This approach to enzyme immobilization was described by Hsuanyu, who reported surprising stability and lifetime of such products compared with conventional porous polymers [11].

Chromatography and Bioprocessing. Large interconnected cavities contained within chemically stable polymer matrices are ideally suited for liquid chromatography applications, including bioprocessing. Because cavities of *Cavilink* polymers are relatively uniform and are individually connected through a network of smaller pores, sample molecules find clear ingress and egress through the matrix, and diffusion limitations characteristic of conventional porous polymers are absent. Thus, mass transfer characteristics are extremely attractive. Separation of proteins and other biopolymers on conventional macroporous polymers occurs only in the outside few angstroms of the spheres. In contrast, because of the interconnections, separation on *Cavilink* polymers occurs throughout the entire volume of beads. Furthermore, since there are no irregular, terminating pores with *Cavilink* polymers, pressure drop through columns of these particles is extremely low. Linear flow velocities of several hundred cm/min are readily accomplished. These properties, and the suitability of such structures for containment and separation of biopolymers, make them ideal candidates for bioprocessing applications.

Drug Delivery. Landgraf *et al.* discovered that certain *Cavilink* polymers exhibit surprising release characteristics [12]. When used as carriers for active pharmaceuticals, these polymers released their contents over a 24-hour period, following near zero-order kinetics. Thus, these materials are ideally suited for providing constant blood levels of many drugs. It appears the zero-order release is independent of drug composition or form, and entirely dependent upon morphology of particular *Cavilink* polymers.

Adhesives. The highly porous nature of *Cavilink* products enables their use as carriers. Capillary forces are quite strong, and will tightly contain many substances for slow release. In some cases, an encapsulation step may be required to ensure long term retention of contained substances. In one experiment, an accelerator component was placed into *Cavilink* spheres, retained, and premixed with an adhesive. The two parts were mixed without fear of reaction since capillary forces prevented viscous liquids from escaping. Later, the reaction was initiated when the beads were crushed or heated to the activation temperature [13].

Catalysis. There are many opportunities for commercial products involving *Cavilink* and catalysis. Any catalytic material attached to *Cavilink* polymer surfaces would have more efficient interaction with reactants due to large cavities and interconnected pores. This unique structure permits reactants to flow into spheres, interact with catalysts, form products, and still allows room for products to flow out and away from newly arriving reactants. Such accessibility of the catalyst to reactants is important for rapid and efficient reactions. This approach was successfully used to catalyze spherical particulates of polyolefins [13].

SUMMARY

Stabilization and synthesis of high internal phase emulsion polymers represent development of the first significant porous polymer morphology in more than forty years. Conventional "macro-porous" polymers, developed in the late 1950s, have led to a variety of products and applications and enjoy wide-spread use. However, irregular pores that terminate in the matrix limit performance and applications of these materials. HIPE polymers, such as *Cavilink* polymers described in this paper, are expected to lead to development of higher performing products and altogether new applications not heretofore possible.

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